THE AMINOCHRONOLOGY OF MAN-INDUCED SHELL MIDDENS IN CAVES IN NORTHERN SPAIN*

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Here, we provide the first report on the ages of 54 archaeological levels in 38 caves in northern Spain by means of the aspartic acid D/L *ratio measurements in* Patella *shells, with good results. For this purpose, we developed an age calculation algorithm that allows the numerical dating of deposits from other archaeological localities in the area and nearby regions. We conclude that the sample size—that is, the number of shells analysed within a single level—reinforces the importance of analysing numerous specimens per horizon and the understanding of the time-averaging concept. The ultrastructure of different species of* Patella *shells was also studied, showing calcite in their apexes and aragonite at their margins.*

INTRODUCTION

Many caves in the northern part of the Iberian Peninsula have provided evidence of human activity during the Palaeolithic, Mesolithic and Neolithic, reflecting an intensive exploitation of molluscs. Sites in Asturias and Cantabria contain archaeological layers dominated by shells of marine molluscs belonging to *Patella vulgata* Linnaeus, *Patella ulyssiponensis* Gmelin, *Patella intermedia* Murray, *Osilinus lineatus* da Costa (*Trochocochlea crassa* Pulteney), *Littorina littorea* Linnaeus, *Mytilus edulis* Linnaeus, *Mytilus galloprovincialis* Lamarck and *Ostrea edulis* Linnaeus. Although some species can be absent, *Patella* shells are present in all localities. In some cases, the land snail *Cepaea nemoralis* (Linnaeus) is also common, as well as animal bones and stone tools (chert and quartzite).

The presence of the large-sized limpet *Patella vulgata* var. *sautuolae*, which in some cases reaches diameters of 50–52 mm (Madariaga de la Campa 1994), together with the winkle *Littorina littorea*, are interpreted as Upper Palaeolithic (especially Magdalenian) indicators. These were substituted in Mesolithic deposits by an association of *Patella intermedia* and *Osilinus lineatus* (typical of warmer waters) (Vega del Sella 1930; Clark 1976; González-Morales 1982,

1996; Arias 1991; Gutiérrez Zugasti 2005, 2006). The increased frequency of *Mytilus galloprovincialis* shells was assumed to be typical of the end of the Asturian (Vega del Sella 1930; Clark 1976); however, González-Morales (1982) considered that the significance of a high concentration of mussels in shell middens should be interpreted in terms of local adaptations to food resources.

Shell middens occur in a variety of forms. Sometimes they are well preserved as uncemented shell piles more than 1 m thick, while in other cases they form a thin layer embedded in archaeological deposits. Middens are usually strongly carbonate-cemented and are therefore preserved from further erosion associated with karst reactivation. In other cases, karst erosion or human activities linked to agriculture have wiped out the main part of the middens and only some shell patches attached to the cave walls or roof survive.

Several dating methods can be used to determine the age of such middens but, until recently, the radiocarbon technique has been almost the only one used for archaeological purposes. In this regard, the ages reported by Clark (1972, 1975, 1976) using the radiocarbon method were definitive for establishing the chronological position of the Asturian. However, in most cases, only a single sample is dated using the ^{14}C method. Moreover, there are some controversies about the age of the Magdalenian/Azilian, Azilian/Asturian and Mesolithic/Neolithic transitions in the north of Spain (cf., Straus 1979, 1981, 1985a,b, 1986; Fernández Tresguerres 1980, 1983; González-Morales 1982, 1992, 1995, 1996; Blas Cortina and Fernández-Tresguerres 1989; Clark 1989; Arias 1991, 1995, 1996; González Sáinz 1994; Strauss *et al.* 2002; Peña-Chocarro *et al.* 2005), mainly because some radiocarbon ages reflect a certain time-overlap.

Among other available dating methods, amino acid racemization (aar) has provided coherent results for determining the ages of archaeological samples in the Iberian Peninsula (Fortea *et al.* 1995, 2003; Torres *et al.* 1997, 2002, 2007).

Living organisms contain only L-amino acids, which gradually racemize into D-amino acids after death. Thus, the D/L ratio increases with time after death until it is equal to 1; that is, when equilibrium is reached. Amino acid racemization provides some advantages over other dating methods. These can be summarized as follows:

(1) Diverse materials, such as mollusc shells (see, e.g., Bada and Schroeder 1972; Kriausakul and Mitterer 1978; Wehmiller and Emerson 1980; Brigham 1983; Kimber *et al.* 1986; Hearty *et al.* 1986; Goodfriend 1987, 1989, 1991, 1992), bones or teeth (see, e.g., Bada 1972; Bada *et al.* 1973; Belluomini 1981; McMenamin *et al.* 1982; Julg *et al.* 1987; Torres *et al.* 2000, 2002), are suitable for this technique.

(2) Only a small amount of sample, between 5 and 10 mg (or even less), is required for amino acid analysis by high-pressure liquid chromatography (HPLC) (Kaufman and Manley 1998).

(3) Many samples from a single bed can be analysed, thereby allowing anomalous results to be identified and time-averaging of the dated event to be calculated (Kowalewski 1996; Kidwell 1998; Kowalewski *et al.* 1998; Behrensmeyer *et al.* 2000; Kowalewski and Bambach 2003).

(4) This method has a greater range than other dating methods, such as the radiocarbon technique. In the Iberian Peninsula the range of the method is ~1.3 Ma (Torres *et al.* 1997; Ortiz *et al.* 2004), but it also works very well for dating Holocene materials (e.g., Goodfriend 1991, 1992; Goodfriend *et al.* 1992, 1995).

Given that amino acid racemization is not a numerical dating method in itself, it requires calibration, mainly with radiometric dating methods. Here, we have established the age calculation algorithm for aspartic acid D/L ratios in *Patella* shells using samples taken from levels that have previously been dated. With the aid of this algorithm, we have determined the ages of numerous archaeological horizons (54) in caves located in northern Spain.

Table 1 *The geographical location of the studied caves, arranged from west to east*

Cave	*Latitude*	*Longitude*	*Elevation a.s.l. (m)*
El Juyo	43°25′54.8″N	3°53′22.4″W	60
Altamira	43°22′40″N	4°07′2.3″W	150
Barra	43°23′34.6″N	4°30′45.0″W	26
Tina 6	43°23′41.6″N	4°30′56.3″W	10
La Cabrera	43°23′50.3″N	4°31′23.2″W	40
Las Madalenas	43°23′47.1″N	4°39′5.4″W	55
Santa Marina	43°23′49.0″N	4°39′27.7″W	45
Entecueva	43°23′54.9″N	4°40′36.3″W	40
Juan de Covera	43°22′58.4″N	4°41′1.8″W	50
Cordoveganes	43°24′8.0″N	4°41′49.3″W	40
Cueto Molino	43°23′4.5″N	4°41′28.7″W	40
Andrín	43°24′7.8″N	4°42′16.0″W	22
Águila	43°23′45.0″N	4°42′30.3″W	50
Sonrasa	43°24′7.4″N	4°42′32.7″W	40
Horadada	43°24′9.8″N	4°42′41.6″W	25
Peña	43°23′6.5″N	4°42′48.7″W	80
Ciernes	43°23′53.5″N	4°42′49.2″W	50
Toral	43°24′3.1″N	4°42′57″W	40
Collamosa	43°23′42.0″N	4°43′10.3″W	45
Colmenera	43°23′43.0″N	4°45′25.3″W	85
Covajorno	43°24′21.6″N	4°46′39.8″W	46
El Quintanal	43°25′50.1″N	4°49′52.5″W	50
Fonfría	43°25′59.5″N	4°50′13.9″W	35
Los Menores	43°25′15.3″N	4°50′41.5″W	42
Mary	43°25′42.7″N	4°50′54.8″W	60
Quintana	43°25′28.1″N	4°50′55.2″W	38
La Riera	43°25′35.9″N	4°51′11.0″W	40
Bricia	43°25′38.2″N	4°51′17.8″W	50
Coberizas	43°25′36.1″N	4°52′40.0″W	50
Cámara	43°22′46.2″N	4°54′45.8″W	110
Llamorey	43°26′50.5″N	4°55′6″W	32
Penicial	43°26′42.9″N	4°56′22.3″W	60
Cuetu La Hoz	43°27′5.1″N	5°2′15.6″W	40
Lloseta	43°27′38.3″N	5°4′29.1″W	40
Ceñil	43°26′20.3″N	5°4′44.2″W	100
Les Pedroses	43°27′26.6″N	5°6′17.7″W	80
Molino	43°28′0.6″N	5°7′47.9″W	40
Carmona	43°28′21.0″N	5°9′6.5″W	80

THE GEOGRAPHICAL SETTING AND A DESCRIPTION OF THE ARCHAEOLOGICAL SITES

The localities in the eastern part of the region of Asturias were sampled during a field campaign in 2006. Limpet shells from the Riera, Altamira and El Juyo caves were provided by M. Hoyos (Museo Nacional de Ciencias Naturales de Madrid). The coordinates of the different localities are reported in Table 1 (see also Fig. 1), together with the period to which the level sampled belongs (Table 2).

Table 2 *Sample references of the archaeological levels and assigned periods*

Cave	*Archaeological level*	*Period*	*Sample*
El Juyo	Level 11 [1]	Lower Magdalenian [1]	JY11-1
	Level 8 [1]		JY8-1
Altamira	Level 2 [2]	Lower Magdalenian [2]	ATM2-1
Barra	Shell midden, *c.* 60 cm thick	Asturian [3, 4]	BAR-1 (top)
			BAR-2 (bottom)
Tina 6	Surface shell midden	Palaeolithic [3–6]	TN6-1
La Cabrera	Surface shell middens, one at the entrance and the other 10 m inside	Asturian [5–7]	LCB-1 (10 m inside)
			LCB-2 (entrance)
Las Madalenas	Surface shell midden, 1.2 m thick	Asturian [4]	LMD-1 (+1 m)
			LMD-2 (+40 cm)
			LMD-3 (+20 cm)
			LMD-4 (bottom)
Santa Marina	Surface shell midden, 30 cm thick	Asturian [4, 5]	STM-1
Entecueva	Surface shell midden (cemented)	Asturian [5, 7]	ENT-1
Juan de Covera	Surface shell midden	Asturian [5, 7–9]	JDC-1
	Black level, 5–10 cm thick	Upper Magdalenian [5, 7–9]	JDC-2
Cordoveganes	Surface shell midden	Asturian [5, 7]	CDV-1
Cueto Molino	Surface shell midden, 40 cm thick	Asturian [5]	CML-1
Andrín	Surface shell midden	Asturian/Azilian*	AND-1
Águila	Surface shell midden (cemented)	Asturian [5, 7, 8]	AGU-1
Sonrasa	Surface shell midden	Asturian [4]	SON-1
Horadada	Surface shell midden	Asturian [4]	HOR-1
Peña	Shell midden, 30 cm thick	Asturian [4, 5]	PEÑ-1
Ciernes	Level, 20 cm thick	Magdalenian?*	CIE-1
Toral	Surface shell midden	Asturian [5, 8]	TOR-1
Collamosa	Surface shell midden	Asturian [5, 7]	COL-1
Colmenera	Surface shell midden	Asturian [5, 6]	CLM-1
Covajorno	Surface shell midden (cemented)	Asturian [4, 5]	COV-1
El Quintanal	Surface shell midden	Asturian [7]	EQI-1
Fonfría	Surface shell midden	Asturian [4, 10]	FON-1 (top)
			FON-2 (bottom)
	Level D [10]	Upper Magdalenian [10]	FON-3
Los Menores	Surface shell midden (cemented)	Asturian [5, 6]	LMR-1
Mary	Surface shell midden	Asturian [4]	MRY-1
Quintana	Surface shell midden	Asturian [5, 8]	QUT-1
La Riera	Surface shell midden	Asturian [11]	RIE-1
Bricia	Cemented shell midden (ceiling)	Asturian [11, 12]	BRI-1
	Shell midden (Level A [16])		BRI-2
	Level C [16]	Upper Magdalenian [12]	BRI-3
Coberizas	Shell midden, 20 cm thick (cut B [11])	Asturian [11]	COB-1
Cámara	Surface shell midden	Asturian [5, 7, 8]	CAM-1
Llamorey	Surface shell midden	Asturian [4, 5]	LMY-1
Penicial	Surface shell midden	Asturian [11, 13]	PEN-1
	Level, 20 cm thick	Magdalenian?†	PEN-2
Cuetu La Hoz	Surface shell midden	Asturian [3, 5]	CLZ-1
Lloseta	Cemented shell midden (sample C [11])	Late Asturian [11]	LLO-1
	Cemented bed above LLO-3	Middle Magdalenian [11]	LLO-2
	Level B (sample A [11])	Middle Magdalenian [11]	LLO-3
	Level C [11]	Lower Magdalenian [11]	LLO-4
Ceñil	Surface shell midden	Asturian [5, 7]	CÑL-1
Les Pedroses	Surface shell midden (cemented)	Late Asturian [11]	LPD-2
	Level, 20 cm thick	Lower Magdalenian [11, 15]	LPD-1
Molino	Surface shell midden (cemented)	Asturian [5, 7, 8]	MOL-1
Carmona	Surface shell midden	Asturian [5, 7, 8]	CAR-1

*New findings.

†In El Penicial cave, only Asturian archaeological remains are described (Vega del Sella 1914; Clark 1976). However, the presence of *Littorina littorea* shells together with big *Patella vulgata* limpets in a thin level suggests that these remains belong to the Palaeolithic (probably Magdalenian) (cf., Vega del Sella 1930): [1], Barandiarán Maestu *et al.* (1987); [2], González Echegaray (1988); [3] Fano (1998); [4], Pérez Suárez (1992); [5], Arias (1991); [6], Pérez Suárez (1982); [7], González-Morales (1982); [8], Gavelas (1980); [9], Vega del Sella, in Utrilla (1981); [10], Vega del Sella (1916, 1930), Obermaier (1916, 1925) and Márquez Uría (1974); [11], Clark (1976); [12], Jordá (1957, 1958); [13], Vega del Sella (1916); [14], Jordá (1958); [15], Hernández-Pacheco *et al.* (1957); [16], Jordá (1954).

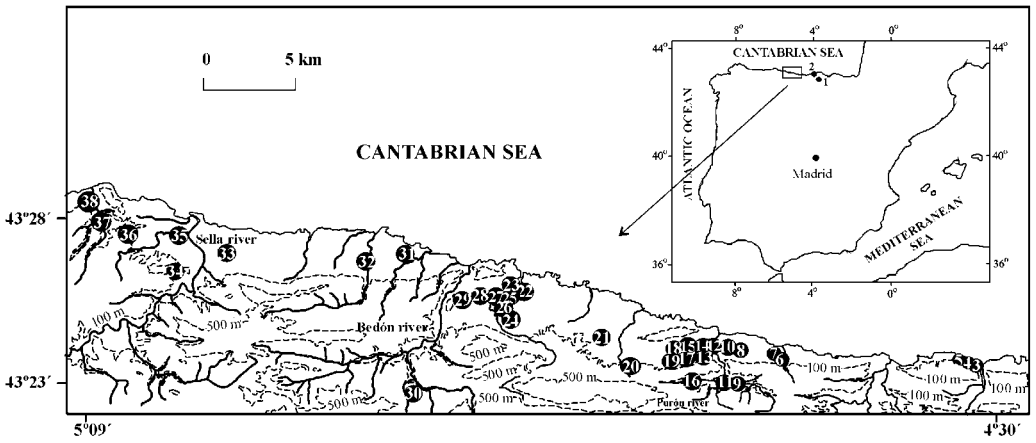

Figure 1 *The geographical locations of the caves studied in this paper: 1, El Juyo; 2, Altamira; 3, Barra; 4, Tina 6; 5, La Cabrera; 6, Las Madalenas; 7, Santa Marina; 8, Entecueva; 9, Juan de Covera; 10, Cordoveganes; 11, Cueto Molino; 12, Andrín; 13, Águila; 14, Sonrasa; 15, Horadada; 16, Peña; 17, Ciernes; 18, Toral; 19, Collamosa; 20, Colmenera; 21, Covajorno; 22, El Quintanal; 23, Fonfría; 24, Los Menores; 25, Mary; 26, Quintana; 27, La Riera; 28, Bricia; 29, Coberizas; 30, Cámara; 31, Llamorey; 32, Penicial; 33, Cuetu La Hoz; 34, Ceñil; 35, Lloseta; 36, Les Pedroses; 37, Molino; 38, Carmona.*

In most caves, only a single archaeological level was observed and sampled; however, in some cases (Barra, Cabrera and Las Madalenas) a number of samples were taken from the same level, or from two or more archaeological levels in the same cave (Juan de Covera, Fonfría, Bricia, Penicial, Lloseta and Les Pedroses).

METHODOLOGY

Petrographic analysis

The mineralogy and preservation of *Patella* shells was studied through petrographic analysis. To distinguish between the two calcium carbonate polymorphs that are usually the mineral constituents of mollusc shells, we applied Feigl's solution to thin sections of *Patella*: aragonite crystals are stained black, while calcite ones remain unstained. In fact, Bailey and Craighead (2003) observed the presence of aragonite and calcite layers in limpet shells with the aid of this solution. Feigl's reagent was prepared following Feigl (1937, in Friedman 1959) as follows: 'solid Ag_2SO_4 is added to a solution of 11.8 g of $MnSO_4 \cdot 7H_2O$ in 100 cm^3 of water and boiled; on cooling the mixture is filtered and one or two drops of dilute NaOH are added and the precipitate which forms is filtered off after one hour'.

Likewise, to better observe the structure of *Patella* shells we submerged them in Mutvei's solution, previously prepared following Schöne *et al.* (2005). One litre of Mutvei's solution consists of 500 ml of 1% acetic acid, 500 ml of 25% glutaraldehyde and ~5–10 g of alcian blue powder. A total of 30 *Patella* shells from distinct localities and belonging to a range of ages (from Lower Magdalenian to present day) were cut into thin sections along their major axes and placed in microscope thin slides. They were then submerged in the Feigl's and Mutvei's solutions for 5 min and observed under a Nikon microscope.

Amino acid racemization

About five or six *Patella* shells (analytical samples)—which were different from those used for petrographic analysis—were taken from each of the archaeological levels. The use of monogeneric samples reduces taxonomically controlled variability in D/L ratios (Murray-Wallace 1995; Murray-Wallace and Goede 1995). Three living limpets were also analysed to establish racemization induced by acid hydrolysis during sample preparation. In the laboratory, shells were carefully sonicated and cleaned with water to remove sediment. Peripheral parts, approximately 20–30%, were removed after chemical cleaning of the sample with 2M HCl.

As several studies (Haugen and Sejrup 1992; Wehmiller 1993; Torres *et al.* 1999) have reported intra-shell variation of D/L ratios depending on the part of the carapace from which the sample is recovered, we perforated a small disc selected from the apexes of all the shells in order to reduce sample error (cf., Murray-Wallace 1995). This selection was also based on the results of the petrographic analysis. Afterwards, ~5–20 mg were selected for amino acid racemization analysis.

Amino acid concentrations and ratios were quantified using HPLC following the sample preparation protocol described in Kaufman and Manley (1998) and Kaufman (2000). This procedure involves hydrolysis, which was performed under an N_2 atmosphere in 7 µl of 6 M HCl for 20 h at 100°C. The hydrolysates were evaporated to dryness *in vacuo*, and then rehydrated in 7 µl of 0.01 M HCl with 1.5 mM sodium azide and 0.03 mM L-*homo*-arginine (internal standard).

Samples were injected into an Agilent HPLC-1100, equipped with a fluorescence detector. Excitation and emission wavelengths were programmed at 335 and 445 nm, respectively. A Hypersil BDS C18 reverse-phase column (5 µm; 250 × 4 mm i.d.) was used for the analysis.

The derivatization takes place before injection by mixing the sample (2 µl) with the pre-column derivatization reagent (2.2 µl), which comprised 260 mM isobutyryl-L-cysteine (chiral thiol) and 170 mM *o*-phthaldialdehyde, dissolved in 1.0 M potassium borate buffer solution at pH 10.4. Eluent A consisted of 23 mM sodium acetate with 1.5 mM sodium azide and 1.3 mM EDTA, adjusted to pH 6.00 with 10 M sodium hydroxide and 10% acetic acid. Eluent B was HPLC-grade methanol and eluent C consisted of HPLC-grade acetonitrile. A linear gradient was performed at 1.0 ml min^{-1} and 25°C, from 95% eluent A and 5% eluent B upon injection to 76.6 eluent A, 23% eluent B and 0.4% eluent C at minute 31.

RESULTS AND DISCUSSION

The thin sections stained with the Feigl's reagent were observed under a petrographic microscope (Fig. 2). In all cases, *Patella* shells (*Patella vulgata*, *Patella intermedia* and *Patella vulgata sautuolae*) showed calcite in their apexes and aragonite at their margins. Therefore, given the similar composition and textural patterns observed in shells of distinct ages, the amino acid D/L ratios in the *Patella* specimens of our study sites can be compared.

According to Goodfriend (1991), the analysis of more than one amino acid provides largely redundant information on sample age. However, to establish the chronology of the archaeological samples, in this paper we used only the aspartic acid content of *Patella* shells, because it is the one that racemizes most quickly. The D/L ratios of other amino acids are not provided because in many cases the D enantiomers could not be identified in the chromatograms (e.g., leucine and isoleucine), or appeared in such low amounts that D/L ratios were not suitable for differentiation between samples (e.g., glutamic acid).

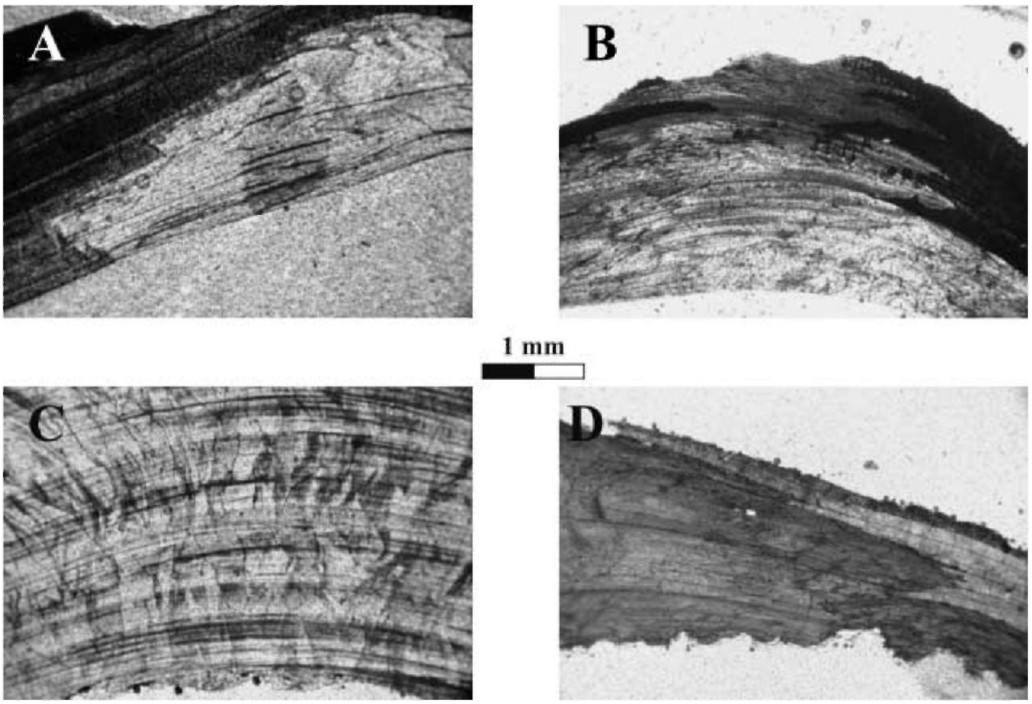

Figure 2 *Microphotographs of thin sections of* Patella *shells treated with the Feigl's (A–C) and Mutvei's (D) solutions: A, apex (unstained) and marginal (black-stained) parts of a living* Patella vulgata *shell; B, apex of a* Patella intermedia *shell from the Asturian shell midden of Penicial cave (note the unstained area in the central part and the black zones at the marginal region); C, unstained apex area of a* Patella vulgata sautuolae *shell from the Lower Magdalenian level (level C) of Lloseta cave; D, apex-marginal area of a* Patella vulgata *shell from the Asturian shell midden of Barra cave (note the transition from the calcite apex area to the aragonite marginal zone).*

The mean aspartic acid racemization ratios of the localities are shown in Table 3. In a few cases, analytical samples provided high L-serine abundances related to the L-aspartic acid and L-glutamic acid contents (two in JY11-1, two in JY8-1, one in JDC-2, one in CLM-1, one in FON-2, one in COV-1, one in QUT-1 and one in CAM-1), indicating contamination by recent amino acids (Kaufman and Manley 1998; Hearty *et al.* 2004) and, therefore, were rejected for the age calculation of these beds.

Racemization is both genus- and temperature-dependent; therefore, these algorithms can be calculated only from samples located in areas with the same thermal history, as in our study sites, which all fall in the same climatic region.

The amino acid racemization method is not a numerical dating method in itself and it requires calibration with either previously dated samples (i.e., through radiometric dating methods) or by 'high'-temperature laboratory experiments to determine the rate of natural amino acid racemization/epimerization in a particular genus. In the former case, two models are commonly used for calibration: first-order reversible kinetics (FOK) and apparent parabolic kinetics (APK); however, other relationships between age and D/L ratios have also been proposed. Nevertheless, since no model satisfactorily describes the patterns of each of the amino acids, a model based on the goodness of fit must be empirically chosen for each data set (Goodfriend 1991). In fact, in the studies by Goodfriend (1991) and Ortiz *et al.* (2004, 2006),

Table 3 *Mean aspartic acid racemization ratios obtained in* Patella *shells from the sampled beds and calculated mean ages*

Sample	*n**	*D/L Asp*	*SD*	*Age (years BP)*
Modern	3	0.037	0.006	0
JY11-1	4	0.361	0.009	15 808 ± 1 065
JY8-1	3	0.351	0.003	14 454 ± 304
ATM2-1	6	0.367	0.024	16 076 ± 2 455
BAR-1	6	0.255	0.015	7 121 ± 964
BAR-2	5	0.252	0.023	6 979 ± 1 539
TN6-1	5	0.370	0.013	16 317 ± 1 317
LCB-1	5	0.234	0.013	5 806 ± 779
LCB-2	5	0.293	0.021	9 795 ± 1 494
LMD-1	5	0.244	0.009	6 399 ± 563
LMD-2	5	0.241	0.019	6 373 ± 1 190
LMD-3	5	0.245	0.012	6 474 ± 765
LMD-4	5	0.279	0.017	8 666 ± 1 138
STM-1	5	0.268	0.012	7 945 ± 776
ENT-1	5	0.297	0.020	10 036 ± 1 489
JDC-1	6	0.298	0.022	10 174 ± 1 753
JDC-2	5	0.339	0.027	13 466 ± 2 365
CDV-1	5	0.226	0.003	5 333 ± 194
CML-1	5	0.262	0.018	7 552 ± 1 178
AND-1	6	0.293	0.014	9 736 ± 1 077
AGU-1	5	0.269	0.020	8 046 ± 1 412
SON-1	6	0.259	0.012	7 263 ± 782
HOR-1	5	0.268	0.006	7 929 ± 424
PEÑ-1	5	0.250	0.017	6 820 ± 1 065
CIE-1	5	0.355	0.011	14 868 ± 1 068
TOR-1	5	0.260	0.034	7 601 ± 2 491
COL-1	5	0.264	0.011	7 638 ± 726
CLM-1	4	0.255	0.010	7 009 ± 614
COV-1	5	0.263	0.014	7 440 ± 955
EQI-1	5	0.232	0.021	5 750 ± 1 209
FON-1	5	0.228	0.008	5 462 ± 493
FON-2	4	0.260	0.020	7 592 ± 1 350
FON-3	6	0.299	0.021	10 219 ± 979
LMR-1	5	0.247	0.026	6 711 ± 1 448
MRY-1	5	0.277	0.014	8 572 ± 1 030
QUT-1	5	0.253	0.030	7 063 ± 1 858
RIE-1	5	0.260	0.009	7 516 ± 588
BRI-1	5	0.281	0.020	8 862 ± 1 403
BRI-2	5	0.256	0.008	7 095 ± 481
BRI-3	5	0.319	0.023	11 773 ± 1 949
COB-1	6	0.255	0.008	6 799 ± 573
CAM-1	5	0.263	0.036	7 878 ± 2 485
LMY-1	5	0.274	0.013	8 329 ± 947
PEN-1	5	0.269	0.013	7 972 ± 885
PEN-2	5	0.347	0.019	14 183 ± 1 678
CLZ-1	5	0.284	0.015	9 101 ± 1 141
LLO-1	6	0.312	0.024	11 256 ± 2 027
LLO-2	6	0.349	0.015	14 293 ± 1 395
LLO-3	5	0.362	0.016	15 565 ± 1 523
LLO-4	5	0.361	0.012	15 423 ± 1 140
CÑL-1	5	0.288	0.015	8 921 ± 1 105
LPD-1	5	0.254	0.015	6 465 ± 928
LPD-2	5	0.365	0.012	15 779 ± 1 179
MOL-1	5	0.247	0.017	6 611 ± 1 093
CAR-1	5	0.295	0.014	9 885 ± 1 094

**n*, The number of *Patella* shells (analytical samples) analysed per sampled level.

Table 4 *^{14}C datings of different archaeological sites in northern Spain. Ages from El Juyo cave (JY7-1 and JY11-1) are in Barandiarán Maestu* et al. *(1987), while the one from Altamira cave (ATM2-1) is in González Echegaray (1988). Ages from Bricia-BRI-2, Riera-RIE-1, Coberizas-COB-1, Penicial-PEN-1, Lloseta-LLO-3 and Les Pedroses-LPD-1 are reported in Clark (1976). All these datings were obtained using a conventional radiocarbon technique. Datings from El Juyo and Altamira caves were calculated on the basis of a ^{14}C half-life of 5638 years (Barandiarán Maeztu* et al. *1987); thus, given that its half-life is 5568 years, we have transformed them using a correction factor of 0.987. The other samples were calculated for a ^{14}C half-life of 5730 years (cf., Clark 1976) and have been transformed using a correction factor of 0.971*

Sample	*^{14}C age (years BP)*	*Material*	*Lab. ref.*
JY7-1	14 261 ± 180	–	I-10738
JY11-1	15 111 ± 690	Carbonized wood	M-380
ATM2-1	15 713 ± 230	Charcoal	I-12012
BRI-2	6 800 ± 165	Charcoal	Gak 2908
RIE-1	8 650 ± 310	Charcoal	Gak 2909
COB-1	7 100 ± 170	Charcoal	Gak 2907
PEN-1	8 650 ± 185	Charcoal	Gak 2906
LLO-3	15 200 ± 140	Charcoal	Gak 2549
LPD-1	5 740 ± 185	Charcoal	Gak 2547

Table 5 *Correlation coefficients* (r) *between time and aspartic acid* D/L *ratios measured in* Patella *snail shells. All correlations are statistically significant at the level of $P < 0.001$. The highest correlation coefficient is shown in bold type*

	D/L Asp	*ln(1 + D/L Asp)/(1 − D/L Asp)*
Time	0.9519	0.9596
Sqrt time	**0.9962**	0.9950

the patterns of several amino acids linearized better with apparent parabolic kinetics, while for others the 'first-order kinetics' trend was the best one.

For calibration of the age calculation algorithms, we used numerical datings of the Altamira, El Juyo, Bricia, Coberizas, Lloseta, Penicial, Riera and Les Pedroses caves obtained by the radiocarbon method (Table 4). As the published radiocarbon dates were calculated on the basis of different ^{14}C half-lives (cf., Clark 1976; Barandiarán Maeztu *et al.* 1987), for comparison they were converted referring to the Libby half-life (5568 years), which is the standard used nowadays.

To select the best fit for the amino-age estimation algorithms, we compared the correlation coefficients (r) for various approaches (Table 5). For this purpose, we used the relationship between the aspartic acid D/L ratio and the square root of time (the apparent parabolic kinetic model, APK), because it provides the highest correlation coefficient. The result (see Fig. 3) is as follows:

$$\sqrt{t} = 378.44 \text{ D/L Asp} - 12.60.$$

Numerical dating is obtained by introducing the D/L aspartic acid ratios of the limpet samples collected in each level into the algorithms (Table 3). The age uncertainty is the standard deviation of all the numerical ages calculated from the amino acid D/L ratios.

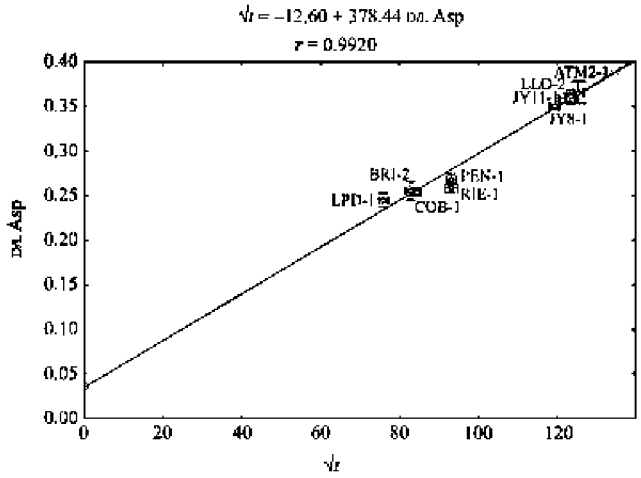

Figure 3 *A plot of* D/L *aspartic acid ratios versus the square root of time.*

In general, the standard deviations of amino acid racemization ages (obtained using five or six analytical samples) were higher than those usually obtained with the radiocarbon method. Traditionally, almost all radiocarbon datings were performed using a single sample, the standard deviation being attributed only to the sampling error. However, when a number of analytical samples from the same horizon are ^{14}C dated, differences as large as 1200 years have been obtained in Mesolithic and Upper Palaeolithic samples (cf., Straus *et al.* 2002; Straus and González-Morales 2003), and even greater differences have been reported (cf., Barandiarán 1988; González Sáinz 1994). Moreover, in some cases, contradictory ages have been shown; see, for example, Tito Bustillo (González Sáinz 1994) or Urtiaga (Altuna 1972, 1979; González Sáinz 1994).

We consider that all processes of 'cultural horizon build-up' represent a time-linked taphonomical process and, therefore, numerical ages must be calculated after time-averaging from many dated samples. The dating of a single sample is only a snapshot of a longer period. In fact, our results highlight the importance of dating numerous specimens per horizon in geochronological studies (e.g., Goodfriend 1989); that is, of dating numerous individuals and using their ages to estimate the mean age of the horizon. This explains the higher values of samples dated by means of the standard deviations of samples dated by means of the amino acid racemization compared to ^{14}C ages, as the former results involve the addition of genus-linked, intra-shell, taphonomical and analytical errors, whereas the radiocarbon technique considers only the analytical error.

Good correspondence was observed between the ages calculated through the amino acid racemization (aar) method and those obtained by the ^{14}C method, except in one case: while the Lloseta-C sample was ^{14}C dated at 4460 ± 309 years BP by Clark (1976), we obtained 11 256 ± 2027 years BP (aar sample LLO-1). However, Clark (1976) states that this sample may be contaminated.

In addition, good correspondence was demonstrated between the period attributed to these archaeological remains and the numerical ages (cf., Tables 2 and 3). In fact, the distinct archaeological levels sampled within the same cave (e.g., Juan de Covera, Fonfría, Bricia, Penicial and Les Pedroses) were distinguishable through the D/L aspartic acid values.

Table 6 *Archaeological sites dated by the ^{14}C method used for the calculation of the density plots of Figure 4. Radiocarbon ages appear in Clark (1976), Fernández-Tresguerres (1980) and references therein, González-Morales (1982) and references therein, Barandiarán Maestu* et al. *(1987), González Echegaray (1988), González Sáinz (1994) and references therein, Utrilla (1996) and references therein, Straus* et al. *(2002) and references therein, and Straus and González-Morales (2003)*

Period	*Archaeological sites*
Lower Magdalenian	Juyo 4, 5, 6, 7 and 11, La Güelga, Beroberría G, Altamira, Caldas XII, Erralla IV and Va, Paloma med, Entrefoces B, Caldas XII inf., and XIII, Rascaño 3, 4.2 and 5, Lloseta A, Altamira – L. Magd., Ekain VIb, Riera 18/19, Castillo 8 inf., Mirón 15 (two datings), 16, 17 (four datings), 19, 20 and 24
Middle Magdalenian	Caldas II, III, IV–V, VIII and IX, Berroberría E inf., Viña IV inf., Abauntz e2, Mirón VIII, 108 (three datings), 110 and 111 (two datings)
Upper Magdalenian	Cueva Oscura IIIA, Castillo 6 (two datings), Urtiaga D, Riera 23 (two datings) and 24, Cueva Oscura IIIA (two datings), Zatoya II, Cueto La Mina B, Berroberría D inf. and E inf., Abauntz e1, Ekain VIb, Rascaño 2.1 and 2.3, Erralla III–II, Caldas I, Paloma sup, Mirón 306, 308, 11.1 and 102.1, Perro 2c, Horno 1, 2 and 12
Azilian	Urtiaga C, Azules I (two datings), 3a, 3d and 3f, Ekain IV-base, Santimamiñe, Arenaza I and II-D, Abrigo Perro 2a, Berroberría D, Arenaza I and III, Cierro, Rascaño 1, Riera 27–28, Piélago 4, El Pendo, Zatoya III and II inf., Mirón 305 and IC (two samples), El Valle I (two samples) and II.2, Horno surface
Asturian	Trecha shell midden (three samples) and 1, Canes D, F and K, Chora, Riera 29 sup and 29 inf, Canes D (two samples), Fragua 1 upp, 1 middle and 1 low sup, Bricia A, Mazaculos A3, 1.1 and 3.3, Coberizas, Sierra Plana, Zatoya II sup, Penicial, Morín 27, Abrigo Perro conchero, Mirón 10.1 (three samples), Ilso de Hayas
Late Asturian	Les Pedroses, Tarrerón III, Lloseta C, Canes and Mazaculos A2

In the Ciernes cave, only one cemented shell midden of Asturian age has been previously described (Pérez Suárez 1992; Fano 1998), which was probably destroyed, as it was not observed during our sampling campaign. Nevertheless, the Magdalenian age obtained through amino acid racemization for a distinct archaeological level located on the floor of the left gallery is consistent with the presence of abundant bones and *Littorina littorea* and *Patella vulgata sautuolae* shells, together with fireplace remains.

To better understand our findings, we performed density plots of the radiocarbon datings of Magdalenian (Lower, Middle and Upper), Azilian, Asturian and Late Asturian (or Post-Asturian) age sites in northern Spain (Fig. 3) in order to compare them with the results obtained in the present study, taking into account the mean and standard deviation values for all samples dated by amino acid racemization. It should be noted that the term 'Post-Asturian' was adopted by Clark (1976), although according to González-Morales (1982) it is better to use 'Late Asturian', as there are no clear cultural differences with the Asturian.

The Fonfría cave deposits attributed to the Magdalenian showed a younger age (10 219 ± 979 years BP) than would be expected; in other words, on the basis of the reviews by González Sáinz (1994), Utrilla (1996) and Aura *et al.* (1998), the Magdalenian extends from *c.* 16 500 years BP to *c.* 11 000 years BP in the north of Spain. However, in accordance with some other radiocarbon datings of Upper Magdalenian deposits (see Fig. 4 and Table 6), it might range below *c.* 10 000 years BP. According to Fernández-Tresguerres (1980), González Sáinz (1994)

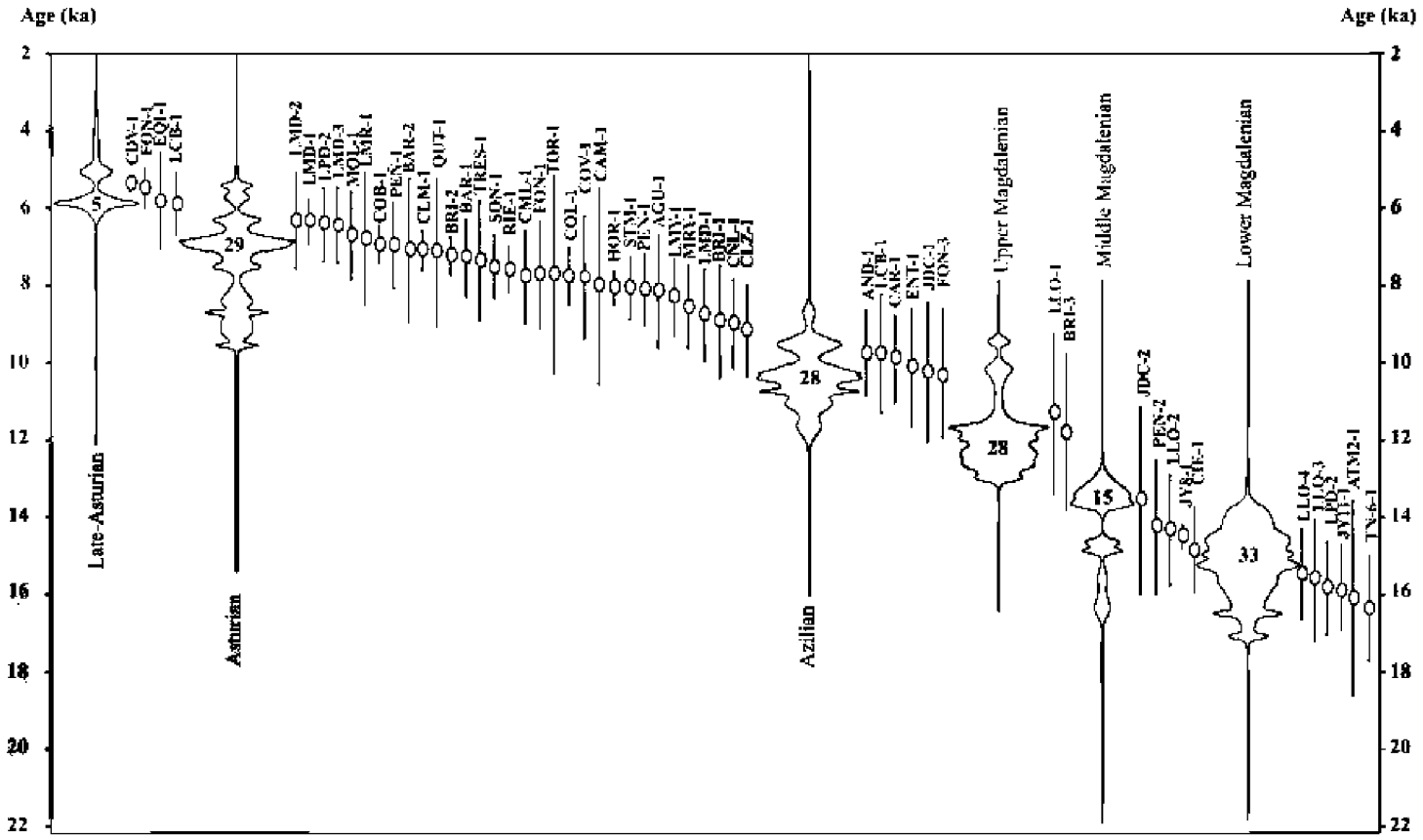

Figure 4 *Means and standard deviations of ages obtained through aspartic acid racemization and density plots calculated using the mean and standard deviation of radiocarbon ages for each period. The sites dated by amino acid racemization are plotted to the right of the corresponding attributed period. The numbers of radiocarbon-dated archaeological sites are shown in the density plots and appear in Table 6.*

and González-Morales (1996), the Azilian ranges between 11 800–11 700 years BP and 9500–9300 years BP, thereby reflecting some time-overlap in the Magdalenian–Azilian transition. In fact, several Magdalenian remains have been ^{14}C dated between 10 000 and 11 000 years BP, although González Sáinz (1994) expressed some objection to some of these 'young' Magdalenian ages. Traditionally, harpoon technology and typology are used to distinguish between these periods.

The Asturian ranges between 9500–9300 years BP and *c.* 6000 years BP (González-Morales 1982, 1996; Fano 1996). A number of authors have previously concluded that the boundary between the Asturian and Azilian is unclear (Straus 1979, 1981, 1985a,b, 1986; Clark 1989), the differences being based on functional rather than cultural aspects. In fact, some radiocarbon datings show contemporaneity of these two groups during the period from 9500 to 8500 years BP (Fig. 4 and Table 6), and according to Straus (1979) the same human groups could be responsible for both cultural entities. In contrast, González-Morales (1982, 1992, 1995), Fernández-Tresguerres (1983), Blas Cortina and Fernández-Tresguerres (1989) and Arias (1991) have described the transition as sharp. Recent excavations have shed light on the functionality within Upper Palaeolithic and Mesolithic sites (Straus 2006), but show clear differences between artefacts and faunal assemblages between cultural periods (Straus *et al.* 2002; Peña-Chocarro *et al.* 2005).

There are also various different points of view regarding the transition between the Mesolithic and the Neolithic. The presence of ceramic remains in some shell middens led Arias (1991, 1995, 1996) to interpret them as belonging to the Neolithic, the transition being progressive, complex and following different rhythms. However, according to González-Morales (1992), there is no evidence to support the existence of a pre-megalithic Neolithic in northern Spain, the beginning of the Neolithic and megalithism being isochronous (Blas Cortina and Fernández Tresguerres 1989). According to Peña-Chocarro *et al.* (2005), Neolithic adaptations were quickly adopted in the Cantabrian region.

On the basis of our findings, we conclude that most of the archaeological remains of the Asturian period cluster between 6500 and 9000 years BP (cf., Table 2 and Fig. 4). However, a number of datings (Entecueva, Juan de Covera-2, La Cabrera-2 and Carmona) reveal that the lower limit could reach *c.* 9800–10 200 years BP and the upper limit (La Cabrera-2 and Cordoveganes) *c.* 5500 years BP. These dates imply that the beginning of the Asturian might be older than expected (cf., González-Morales 1982) or that the stratigraphy of these deposits should be revised. In this regard, the calculation of radiocarbon ages around 10 000 years BP can be problematic because of the observed plateau in the radiocarbon time-scale at this date (cf., Becker and Kromer 1986). However, given the standard deviations of these datings, they could be placed either in the Asturian or the Azilian.

CONCLUSIONS

Here we have shown that the amino acid racemization analysis of *Patella* shells from archaeological sites located in northern Spain is an efficient tool for numerical dating purposes. The sample size (the number of individual shells analysed within a single bed) has allowed us to reject anomalous results before age calculation, and reinforces the importance of understanding time-averaging.

We have established the age calculation algorithm for D/L ratios of aspartic acid in limpets and this allows the numerical dating of deposits from other localities in the area (i.e., Cantabria and the Basque country). We provide the first report of amino acid racemization to determine the ages of 54 archaeological levels in 38 caves in northern Spain.

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